Optically induced anisotropy of surface plasmons in spherical metal nanoparticles

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Red shift and splitting of surface plasmon band in absorption spectra of copper nanoparticles incorporated in silica matrix have been observed under irradiation by intense femtosecond laser pulse with power density $10^{11}-10^{12}$ W/cm^2. These phenomena are interpreted as a result of change of dielectric constant of the silica matrix and its induced anisotropy due to optical Kerr effect in the electric field of light wave enhanced in the vicinity of the metal nanoparticles. Suggested interpretation is supported by the results of pump-probe measurements in different polarizations. After the end of pump pulse plasmon shifts to the blue side. This blue shift is also polarization dependent and it can be attributed to formation of plasma in silica around nanoparticle.

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Study of surface plasmon in nanostructures and its interaction with intense electromagnetic field is important topic in spectroscopy of solids because of its significance both for pure and applied surface science. This interest is caused by a number of specific phenomena observed at the surface of metal in pico- and femtosecond time domain and also by promising applications in the emerging fields of nanophotonics and plasmonics. But most of the studies (see for example Refs. 1 and 2) are concentrated on laser-induced changes in electron gas in metal and energy transfer between electrons and lattice. Usually only changes of integral characteristics of the sample, i.e., transmittance or reflectance, are studied. In present paper we study spectral characteristics of surface plasmon resonance, particularly its fine structure, which appear in intense electromagnetic field of laser pulse. As a result we report observation of splitting of surface plasmon resonance frequency in spherical copper nanoparticles under laser irradiation, which can be attributed to laser-induced anisotropy in dielectric constant of silica matrix. This splitting appears due to optical Kerr effect and enhancement of electric field at the surface of metal nanoparticles.

Samples containing spherical copper nanoparticles with narrow size distribution in pure silica matrix have been prepared by modified sol-gel method.[3] High optical quality of the samples and high stability of silica allowed measurements at higher intensities of pump beam in pump-probe measurements compared to other studies.[1,2]

Pump-probe measurements have been performed with a Coherent femtosecond laser system consisting of a Mira-900F oscillator operating at 800 nm and a Legend HE amplifier. Output pulse energy was 2 mJ at 1 kHz repetition rate. Pulse duration was approximately 130 fs, estimated from autocorrelation function. Probe "white light" was generated in a sapphire plate. As a pump beam we used part of amplifier output attenuated to desired intensity by neutral density filters. Pump and probe beams were focused on the sample with long-focus lens. Spectrum of the probe transmitted through the sample was analyzed with an Acton SP500i spectrometer equipped with a SPEC-10 CCD detector.

For polarization measurements "white light" probe beam was generated from laser beam with plane of polarization at 45° to that of pump beam. Required polarization of probe beam (parallel or perpendicular to polarization of pump) was selected with a polaroid film. To avoid bleaching of polaroid film it was placed after blue filter which cuts off 800 nm fundamental laser radiation. Usage of film polarizer eliminated variation of probe pulse delay for different polarizations and its temporal broadening comparing to inherent such variations in case of usage of a polarizing prism. Measurements were performed at room temperature.

Characteristic feature of absorption spectrum of copper nanoparticles is absorption peak of surface plasmon at 2.17 eV. Under intense pump it decreases in amplitude and broadens. Thus at the location of initial plasmon peak the induced transparency is observed while optical density increases at the wings of plasmon peak. Temporal evolution of characteristics of electron gas in nanoparticles can be studied in the first approximation from kinetics of induced transparency at plasmon peak. It was found that induced transparency demonstrate two-exponent decay with time constants of about 2.5 and 300 ps, fast component reflects energy transfer from electron gas to lattice and slow component corresponds to energy transfer to silica matrix.[4]

More details can be obtained from analysis of the shape of plasmon peak and its evolution during and after pump pulse (Fig. 1). In this figure plasmon peak is shown without background caused by band-to-band transitions in copper. Spectra measured with different time delays are displaced vertically for clarity. Delay time indicated at the right of each spectrum is measured from the center of pump pulse. At first, red shift of plasmon is observed for very short time approximately equal to pump pulse duration. After the end of pump pulse plasmon peak shifts to blue side and then gradually relaxes to original position with time constant $\tau \approx 1.1$ ps. These phenomena have been reported in Ref. 4 and explained in Ref. 5 taking into account changes of the dielectric constant of both silica matrix and copper nanoparticles, electron transitions in copper and plasma formation in silica.

Another interesting feature that we report in present paper is splitting of surface plasmon peak (Fig. 1) clearly observed at high intensity of pump beam of the order of 10^{12} W/cm^2. For its explanation one can recall that interaction of light

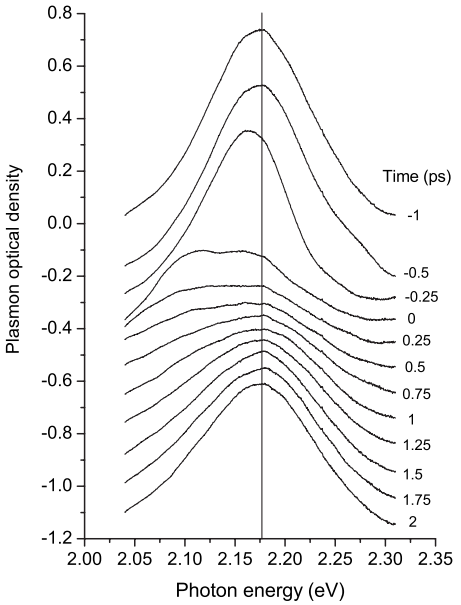

FIG. 1. Splitting of plasmon peak in copper nanoparticles with $d=50$ nm under 800 nm, 70 mJ/cm^2 pump. Spectra obtained at different delays (indicated at the right) are displaced vertically for clarity.

with metal nanoparticle has mainly dipole character. As a result area with enhanced electric field induced in the vicinity of nanoparticle has specific uniaxial symmetry with maxima at the poles of nanoparticle. It causes induced anisotropy of silica matrix surrounding nanoparticle and leads to splitting of surface plasmon resonance similar to splitting in anisotropic shape (elliptical) nanoparticles[6,7] or in spherical metal nanoparticles incorporated into anisotropic matrix.[8] We have checked this supposition by pump-probe measurements with different polarization of probe beam (Fig. 2). Significant difference of plasmon peak shift in different polarization is observed during pump pulse. This difference in shift value leads to splitting observed in nonpolarized light (Fig. 1).

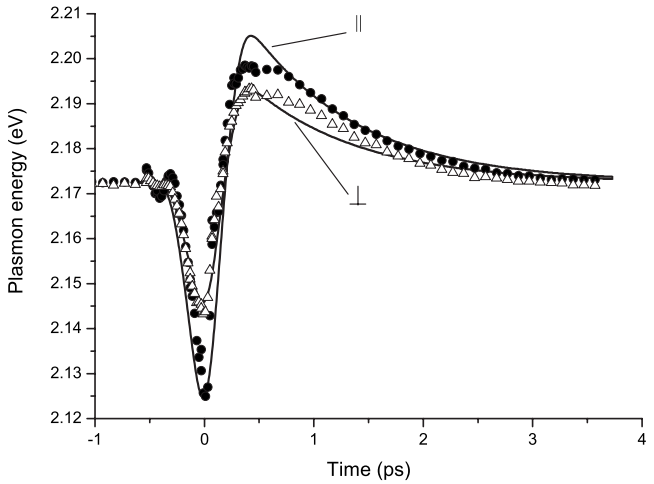

FIG. 2. Shift of plasmon peak observed with probe light polarized parallel (closed circles) and perpendicular (open triangles) to polarization of pump beam. Lines present the results of theoretical calculations.

At the end of pump pulse spectral shift of plasmon quickly changes its sign (Fig. 2) and gradually relaxes to its original position with time constant 1.1 ps. Two possible explanations for the observed blue shift have been suggested:[4,5] increase of free electron concentration in copper or formation of plasma in silica. Both phenomena can cause increase of plasmon frequency and likely should have similar kinetics. One can doubt about possibility of plasma formation in silica under present experimental conditions. Usually plasma formation is observed at higher intensities of the order of $10^{13}-10^{14}$ W/cm^2 (Refs. 10 and 11) but taking into account field enhancement it can happen in present experiment. Also plasma formation can be stimulated by electron emission from copper nanoparticles. The supposition of plasma formation around nanoparticles is supported by polarization dependence of blue shift (Fig. 2).

From the kinetics of plasmon blue shift we can estimate lifetime of plasma in silica matrix as approximately 1 ps. This value is larger than reported for silica in most papers.[10,12–14] Note, however, that experimental data on the plasma lifetime in fused silica are contradictory (150 fs in Refs. 12 and 14, 170 fs in Ref. 13, 250–330 fs in Ref. 15, and 15 ps in Ref. 11). Difference can be attributed to difference in structure of silica prepared by different methods. In our samples silica matrix is obtained in complicated route of sintering of silica nanopowder with products of decomposition of tetraethoxysilane.[3] Remaining grain boundaries can slow down plasma relaxation. Possible presence of free electrons injected from copper nanoparticles into matrix can also increase plasma lifetime.

The key to explanation of the observed splitting of surface plasmon band is in the instantaneous character of this splitting. That leads to assumption that optical Kerr effect is the phenomenon responsible for the splitting. However, because of small value of n_2 in silica (according to[9] $n_2=2.48\times10^{-16}$ cm^2/W) observed large values of plasmon red shift and consequently its splitting can be explained only taking into account electric field enhancement in the vicinity of metal nanoparticles:[5] $E_1=G\ E_0$, where E_0 and E_1 is electric field of incident electromagnetic wave in silica far from nanoparticles and in the vicinity of copper nanoparticle, respectively. It causes change of dielectric constant ϵ_m and refraction index n_m of silica matrix surrounding nanoparticle $n_m=n_0+n_2I_1$, where $I_1=\frac{cn_mE_1^2}{8\pi}$. As a result frequency of surface plasmon Ω_{SP} determined as

$$\Omega_{SP}=\frac{\omega_p}{\sqrt{\epsilon_{b1}(\Omega_{SP})+2\epsilon_m}} \tag{1}$$

decreases. Here ω_p is plasma frequency of bulk copper, $\epsilon_{b1}(\Omega_{SP})$ is contribution of bound electrons to dielectric constant of copper.

And since intensity of electromagnetic wave around copper nanoparticle has no spherical symmetry, changes of dielectric constant of silica and corresponding changes of plasmon resonance frequency demonstrate anisotropy with axis

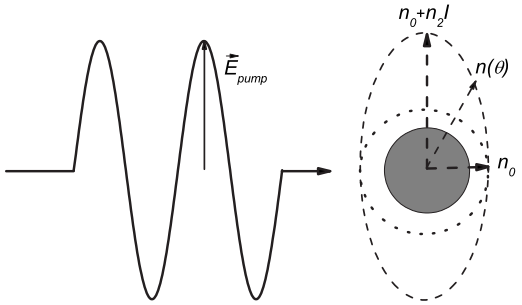

FIG. 3. Simplified schematic of interaction of electromagnetic wave of pump pulse with metal nanoparticle. Dotted circle and dashed ellipse represent cross-sections of indicatrix $n(\theta)$ of refractive index of silica (not to scale) at the surface of nanoparticle in the initial conditions and in presence of pump pulse, respectively.

determined by polarization of the pump beam (Fig. 3). To calculate the influence of induced changes of dielectric constant of matrix on plasmon resonance frequency for different polarizations of probe light we have to consider details of interaction of plasmon electric field with matrix. It is natural to suppose that such influence is stronger in the areas where the electric field of plasmon is larger. Thus, total effect should be proportional to the product of change of dielectric constant $\Delta\epsilon_m$ and plasmon electric field E_{SP} integrated over the volume around nanoparticle. And also we have to take into account that Kerr effect induces birefringence, i.e., change of dielectric constant is the largest in the direction of the electric field that causes Kerr effect (pump field). Finally, for the change of plasmon resonance frequency [Eq. (1)] we can suggest

$$\Delta\Omega_{SP} \propto \frac{\int \left(\sum_{i=1}^{3} [\Delta\epsilon_m^i(\mathbf{r}) E_{SP}^i(\mathbf{r})]^2 \right)^{1/2} dV}{\int \epsilon_m(\mathbf{r}) E_{SP}(\mathbf{r}) dV}, \tag{2}$$

where superscript i denotes x,y,z components, $\Delta\epsilon_m^i$ is determined by pump field enhanced and distorted in the vicinity of nanoparticle. For homogenous polarization of sphere we can take it as field of dipole $\mathbf{p}$,

$$\mathbf{E} = \frac{3(\mathbf{rp})\mathbf{r}}{r^5} - \frac{\mathbf{p}}{r^3}. \tag{3}$$

Field of the probe plasmon $E_{SP}(\mathbf{r})$ is also taken as the field of a dipole oriented parallel or perpendicular to polarization of the pump beam. Difference of the integral overlap [Eq. (2)] of these two fields causes difference of plasmon red shift observed in two polarizations.

Similar considerations can be applied to explanation of the plasmon blue shift tentatively attributed to formation of plasma in silica around nanoparticle that causes decrease of dielectric constant of silica

$$\Delta\epsilon_m = -\frac{Ne^2}{\epsilon_m m^* \omega^2}, \tag{4}$$

$$\Delta\Omega_{SP} \propto \frac{\int \Delta\epsilon_m(\mathbf{r}) E_{SP}(\mathbf{r}) dV}{\int \epsilon_m(\mathbf{r}) E_{SP}(\mathbf{r}) dV}, \tag{5}$$

where N is plasma concentration, m^* is mass of charge carriers. Difference with Kerr effect is absence of birefringence and kinetics determined by the processes of plasma generation and relaxation,

$$\frac{dN}{dt} = \alpha[I(t)]^6 - \beta N - \gamma N^2, \tag{6}$$

where $I(t)=I_0 \operatorname{sech}^2(\frac{1.76t}{\tau_p})$ is intensity profile of the pump pulse τ_p. Here plasma generation is taken proportional to the 6 power of intensity according to the ratio of the silica band gap and the pump photon energy. Equation Eq. (6) has analytical solution but it is too bulky to be presented in the paper. For numerical calculations we neglect quadratic recombination of plasma γN^2 according to experimental data,[16] which indicate that in silica linear relaxation term βN prevails. The results of numeric calculations of kinetics of plasmon resonance frequency, which take into account both Kerr effect [Eq. (2)] and plasma excitation [Eq. (5)], are presented as solid lines in Fig. 2 for two polarizations of the probe pulse. For correct comparison with experimental data convolution of calculated kinetics with white light pulse $I_{wl}(t)=I_0 \operatorname{sech}^2(\frac{1.76t}{\tau_{wl}})$ is performed. Obtained curves demonstrate good agreement with experimental data. It should be emphasized that no fitting was performed for the ratio of plasmon shifts in different polarizations, presented values come directly from the ratio of integrals Eqs. (2) and (5) for different polarizations of probe light.

Optically induced anisotropy of surface plasmon in copper nanoparticles is observed under irradiation by intense femtosecond laser pulse. Red shift of surface plasmon in copper nanoparticles and its splitting into two components during pump pulse indicates Kerr-induced changes of the dielectric constant of silica matrix. After the end of pump pulse plasmon shifts to blue side and broadens. The blue shift is attributed to formation of plasma in silica matrix. Subpicosecond kinetics of plasmon shifts and induced anisotropy may be useful for applications in optical switches and ultrafast sensors.

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